Minimization of the environmental impact of chrome tanning: a new process with high chrome exhaustion

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Abstract

In all tanning technology operations wastes are generated. These reach the environment as residual waters, solid and liquid waste as well as atmospheric emissions and odours.

This study tests an alternative method to the traditional tanning method at an industrial level. The new method is based on tanning without float and by significantly increasing the temperature at the end of the tanning process. The properties of the leathers obtained using the two methods have been compared and the results indicate that those leathers have similar physical, chemical, and organoleptic properties. However, the differences existing from the environmental point of view are significant. It is not necessary to use clean water for this tanning. Moreover, there is a 75% reduction of the residual float, a 91% reduction of the chrome discharged, and a 94% reduction of the chlorides discharged. A financial assessment was carried out to demonstrate that the newly proposed system is 32% more economic than the traditional one.

Keywords

Tanning industry, chrome tanning, chrome exhaustion, salinity, tanning wastewater, residual float.

1. Introduction

The paper deals with the environmental concerns generated by the tanning industry and focuses on chrome tanning, one of the most polluting parts of the process. This operation involves preparing the hides with acid and salt and subsequently tanning them with chromium salt (Heidemann, 1993; Morera, 2000). This entails using large quantities of clean water that will end up being transformed into highly contaminant waste water (Simpson et al., 2001; Saravanabhavan et al., 2003; Thanikailevan et al., 2004). In order to provide an estimate of the amount of water involved in the process, the latest studies by official organisations (FAO, 2006) estimate that approximately 6 Mt of bovine salted raw hides are tanned yearly worldwide. Approximately 90% of these hides are tanned using chrome. In accordance with the pollution values from tannery processes under conditions of good practice (IULTCS, 2006), there is an average estimation that chrome tanning results in approximately 11 million m^3 of contaminated water yearly, containing approximately 0.22 Mt of salt and approximately 0.02 Mt of Cr(III).

Although alternative paths have been explored regarding the working processes, the traditional system has not yet been improved. Unfortunately, most of the solutions proposed have not taken into account the possibility of saving water during the tanning process. Although there are other chemical products to tan the leather, the result obtained is not the same and there is no indication that chrome will be less relevant in the near future.

In order to carry out the chrome tanning, the hides are immersed in a saline dissolution at acidic pH. The presence of salt in the dissolution is necessary to prevent the hides from swelling because of the acidity resulting from the process and the chrome from penetrating the hides. The process takes place inside some cylindrical containers called drums. By rotating on their axis, the drums provide the necessary agitation for the chrome to be absorbed by the hides. The main component of the hide is a protein called collagen. Once the chrome has been absorbed by the hides, gets fixed to the collagen by an increase in the pH. This stabilises the protein against putrefaction. It is considered that at this point the hide has become leather. Unfortunately, the tanning results in a residual float that contains high amounts of chrome and chlorides.

Different systems have been proposed in order to minimize the negative effect of such pollution, but without rejecting the use of chrome as a tanning material. These systems are, for instance, recirculation and/or recycling of tanning floats (Cranston et al., 1997; Aloy and Vuillermet, 1998; Tobin and Roux, 1998; Song et al., 2000; Scholz and Lucas, 2003) as well as processes with high chrome exhaustion (Luck, 1980; Mayer, 1981; Francke, 1991; Fuchs et al., 1993). These systems help to minimize quite effectively the discharge of chrome, but neither the water consumption nor the salinity that results from the process is rarely taken into consideration. However, it is possible to modify the manufacturing process in order to simultaneously minimize the three parameters mentioned above (Pelckmans and Püntener, 2005).

The modification developed in this study is based on the following assumptions:

a) Before tanning, the hide is subjected to many other operations with the intervention of water. The hide retains part of this water. As a result, the amount of water absorbed by the hide before the start of the tanning process is enough to dissolve the solid chemical products used in the tanning.

b) The salt is necessary to prevent the swelling of the hides at the working acidic pH. As a result, the amount of added salt will be greatly reduced when working without float.

c) An increase of temperature during the chrome fixation results in improvements of the reaction. Working without float favours an increase of temperature which can be controlled in accordance with the speed at which the drum rotates. The greater the amount of chrome fixed to the hide, the greater the reduction of chrome content in the residual float.

2. Materials and methods

2.1. Material

The tests were carried out using 2.2 m-high (i.e. diameter) and 2.2 m-wide wood drums (Fig. 1). Bovine salted hides were used in order to perform the tests. 1800 kg of split hides at 3 mm were processed in each test. The chemicals used in the operations were those normally used in the leather industry. The chemicals used for analytical analysis were of laboratory grade.

2.2. Methodology

The hides were first soaked, then unhaired using 2% sodium sulphide and 3.5% lime, fleshed and split at 3 mm. In order to finish the preparation before tanning, the hides were delimed with 1.5% of a commercially available carboxilic acid and were bated with 0.7% of enzymes of 1,000 LVU g^{-1}. The pH of the hides at the start of the tanning was 8.5. The formulations used in the tanning are shown in Tables 1 and 2.

In the tanning carried out without float, and precisely because of the lack of a significant mass of water, the temperature increased progressively and the tanning finished at 55 ºC. In contrast, in the tanning with float the temperature was at 30 ºC.

In order to determine the quality of the leathers and to compare the two systems, we carried out the physical tests set up by the IULTCS, which allowed us to assess the capacity of the leathers to withold the wear and tear of the leather goods, shoes, and garments. The following official IUP methods were used to this end:

IUP 6 Measurement of tensile strength and percentage elongation (IUP 6, 2000). To carry out this test a leather sample is fixed on the clamps of a dynamometer. Then the clamps are subsequently separated at a constant speed while the force exerted on the sample is measured with the load cell of the device. The elongation is calculated as the difference between the final and initial separation of the sample. This difference is expressed as a percentage of the initial separation.

IUP 8. Measurement of tear load (IUP 8, 2000). This method is used to determine the capacity of the leather to withhold multidirectional tensions. In order to perform this test the dynamomenter is also used by fixing a leather sample with a slot and subsequently separating the clamps at constant speed, causing the leather to tear completely.

IUP 9. Measurement of distension and strength of grain by the ball burst test (IUP 9, 1960). This test assesses the performance of the leather in the upper side of the shoe by using a lastometer, a machine developed by SATRA. The leather is progressively deformed until the first crack appears, acquiring thus a conic shape. Action is not stopped until total break takes place.

IUP 16. Measurement of shrinkage temperature up to 100 ºC (IUP 16, 2000). Shrinkage temperature is a parameter of great importance to measure the degree of stabilization of collagen in leather. It is determined by immersing a strip of leather in a mixture of water and glycerin subjected to a slow temperature increase. Shrinkage temperature is therefore the temperature at which shrinkage of the leather takes place.

In addition, for the purpose of assessing the pollution in wastewaters and chrome fixation the following standarized chemical methods recommended by IULTCS are applied:

IUC 8. Determination of chromium oxide content (IUC 8, 1998). To quantify the amount of chromium fixated on the leather the oxidation-reduction volumetric analytical method is used.

UNE-EN 1233:1997. Water quality. Chome determination. Methods of atomic absorption spectrophtometry (UNE 1233, 1997).

UNE 77041:2002. Water quality. Chloride determination. Argentometrical method (UNE 77041, 2002).

The physical tests and the chemical analyses were carried out on both the leathers and the floats once the leathers had been fully processed.

The leathers in each of the tests were piled separately. A panel of five experts examined each of the piles without knowing what kind of tanning process had been applied. The experts compared the organoleptic properties of the leathers, informed about the differences between the different piles and calculated their commercial value.

In order to carry out a study on the financial feasibility, the changes in expenses in tanning with or without float were considered since the remaining operations in the whole process are identical. These changes mainly relate to the water supply, the chemical products used for tanning and the wastewater from tanning and draining. In Igualada, this wastewater is processed in a plant for chrome recovery. The fees from that plant have been considered in the estimate of the costs. Despite having analyzed the chrome content in the residual floats of the operations conducted after tanning, they have not been considered in the estimate of the costs. The reason for this is that such operations may vary considerably depending on the manufactured goods. Even though the estimate of the costs would still favour the system without float, it was decided that it made more sense to restrict such an estimate to the most important and unchanging operations: tanning and draining.

3. Results and discussion

3.1. Effect of new process on tanning effluent quality

Five tanning trials were carried out with the system without water addition. A series of physical tests and chemical analyses were conducted on the leathers obtained. The amount of residual float was also controlled. The float resulted from the tanning and from the operations conducted before the leather dried up. The residual float was analyzed in order to determine the amount of chrome and the salinity it contained. Five further tanning were carried out using the traditional system. The same tests were repeated on the hide and in the residual float. The results obtained and the average standard deviation are shown in Fig. 2 and Fig. 3. Once the tanning process had finished and the leather obtained was suitable for commercialization as leather goods, a panel of five experts looked for any possible changes in its organoleptic properties (grain smoothness, feel, etc.). Finally, an estimate of the costs was calculated in order to assess the sustainability of the new process. A comparison of the costs between the suggested system and the traditional one is shown in Fig. 4.

The results indicate that, regardless of the system used for tanning, the properties of the leathers are similar. A significantly different result was obtained when the chrome absorbed by the hide was analysed. Thus, the system without water allows the hide to absorb much more chrome. This improvement in Cr_2O_3 fixation is both due to the simmultaneous effect of the rise in final temperature to 55 ºC and to operating without any addition of bath. The temperature increase facilitates the formation of chrome complexes and also increases the speed of creation of new complexes with the reactive points of collagen. Also, working with no addition of bath enables an increase of the mechanical effect, which contributes not only to improving the penetration of chrome into the leather but also to increasing the speed of chrome fixation by increasing the concentration of the solution. Since the addition of chrome in the two types of tanning is the same it indirectly points to the supposition that the residual chrome obtained will be greatly reduced. This was confirmed by the results obtained from the analysis of the residual floats in the tanning and the further operations that were carried out. Using the system without float, 91% less residual chrome is obtained from the tanning and draining operations. This amount goes up to 92% if we also consider the residual floats from further operations.

There is also a sharp decrease in the chloride discharged using the system without float due to the lower addition of salt. In percentage terms, this decrease in the amount of chlorides discharged is 94%. It is worth pointing out that the chrome and chloride values obtained after using the traditional tanning system are lower than the average values provided by official organizations (IULTCS, 2006). The reason for this is that the tanning had been carried out aiming to minimize the amount of resulting waste. If the traditional tanning had been carried out without such control, the percentages of chrome and chlorides would have been higher. These steps guarantee thus that the following figures, calculated from the bibliographic data mentioned before and the percentage of reduction of pollutants found in conducting the experiment, either resemble the real values or are only a little lower. We must stress that the traditional process was carried out at 30 ºC although depending on the variability of the season and climate of the location of the tests the temperature inside the drum could reach 38 ºC. The new process has been compared to the traditional one at 30 ºC, since in previous studies it was observed that the qualitative differences regarding chrome exhaustion do not occur unless working conditions reach temperatures of or over 45 ºC. (Bacardit, 2005). Chrome exhaustion produced when finishing the tanning at 38 ºC is very little compared to the differences obtained in this current study after increasing the temperature to 55 ºC. The absence of water in the process is the factor that enables to reach a temperature of 55 ºC inside the drum.

Another saving worth mentioning is the water supplied. As in the previous instance, it is a result of the system used in the tanning. With the system without float there is a saving of 0.7 m^3 of water per t of processed split hide. This means that if the system without float was applied elsewhere worldwide, there would be a saving of more than 4 million m^3 of water per year. At the same time, the residual chlorides would be reduced by approximately 0.2 Mt, and the residual chrome by approximately 0.018 Mt.

With regard to the decrease in chrome being discharged, the results obtained agree with those from other recent studies (Rivela et al., 2004; Thanikaivelan et al., 2005; Saravanabhavan et al., 2006). Moreover, the "Best Available Techniques" report written by European Union experts (European Commission, 2003) demonstrates that a 90% chrome uptake can be achieved by altering effortless operational parameters – raising the temperature to 50 ºC, adjusting pH to 4.5 and controlling the float level – or by addition of new chemicals. The EU report also indicates that a decrease in the tanning float leads to grain damage, which renders it unusable for high-quality leather goods. However, our study demonstrates the opposite: that it is indeed possible to dispense with the float and not damage the grain. This outcome was possible due to the chromium salt mixture and the basification system we used. We manipulated these two variables to achieve a rapid penetration, even distribution and high fixation of chrome at relatively low pH values. The result was a smooth, thin grain. Rough grains due to basification at higher pH values were thus avoided.

3.2. Effect of new process on leather properties

In relation to the organoleptic properties, the panel of experts agreed that the tanned leathers had a fuller and softer feel. This is a direct consequence of higher chrome absorption by the hide. As for the remaining properties, it was demonstrated that, regardless of the system used, there were practically no differences in quality or in market price among the manufactured leathers. Thus, it is only fair to think that if the amount of chrome absorbed by the hide in the system without float addition was adjusted, then it would be easy to obtain a leather almost identical to the one obtained using the traditional system. Such a consideration leads to another potential saving: the possibility of reducing the addition of chrome in the tanning process in order to obtain leather with the same amount of chrome absorbed as that of the traditional system. This has to be taken into consideration, although it depends on further investigation since the working conditions using the system without float are potentially more damaging for the leather (i.e. its protein structure can be further damaged) than using the traditional system. It might be that a minimum amount of chrome addition is required in order to carry out the tanning satisfactorily.

3.3. Economical considerations

For a process to be considered sustainable it must offer environmental improvements and it must be economically feasible.

The price of waste water has been calculated on the basis of the current price paid by tanners in Igualada (Spain) to get their waste water to a chrome recovery plant. This involves savings of 45.32 € per ton, which is equivalent to 32% approximately. The price of water supply and the chemical products used are also calculated in accordance with the data provided by five tanning factories from Igualada.

The results indicate that the tanning system without float is more economical than the traditional one. It must be pointed out that the adoption of the system without float does not entail any kind of investment or additional expense. It does not have to result in changes in the working plans of a factory either. In Spain at least, there is a tendency towards an increase in prices and taxes regarding the water and its treatment. It is thus fair to assert that the savings estimated in Fig. 4 will be increasingly significant in years to come.

4. Conclusions

The aim of this study was to check the advantage of introducing an alternative method to the traditional tanning system based on tanning without using clean water, reducing the amount of salt and finishing the tanning at 55 ºC. The conclusions are as follows:

(1) The tests conducted at industrial plant level suggest that a modification of the traditional chrome tanning process without float results in leathers with a similar quality to that obtained using the traditional tanning system.

(2) The new tanning system results in considerable savings in water supply and a great reduction of the residual float (75%), the chrome content (91%) and the chlorides discharged (94%).

(3) The change in system reduces the tanning expenses by 32%.

(4) The suggested modification implies an improvement regarding both the environmental and the economical aspects, and its application would increase the sustainability of the tanning process.

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Fig. 1.

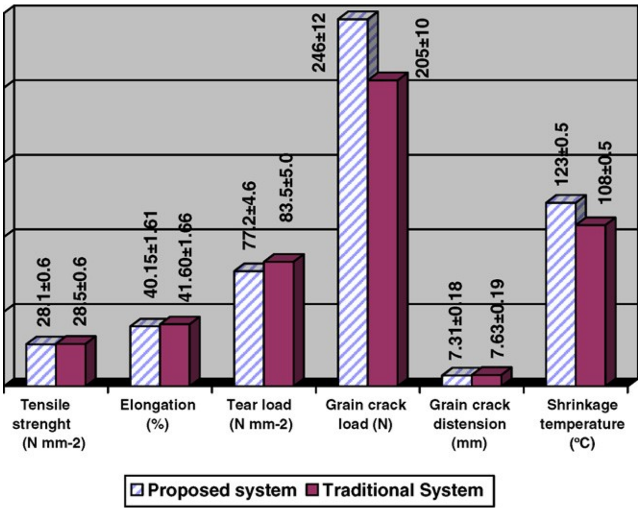

Fig. 2. Physical tests comparison.

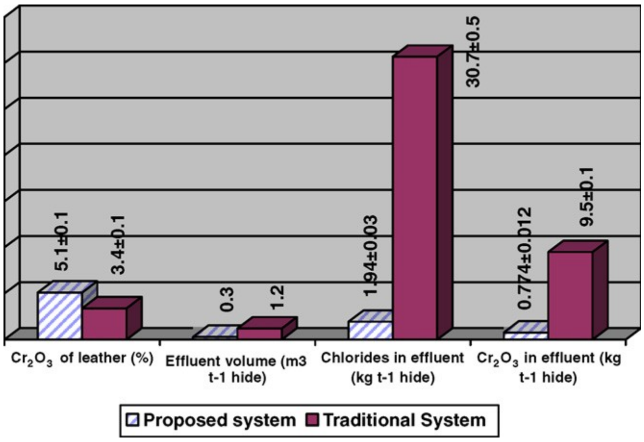

Fig. 3. Chemical analyses

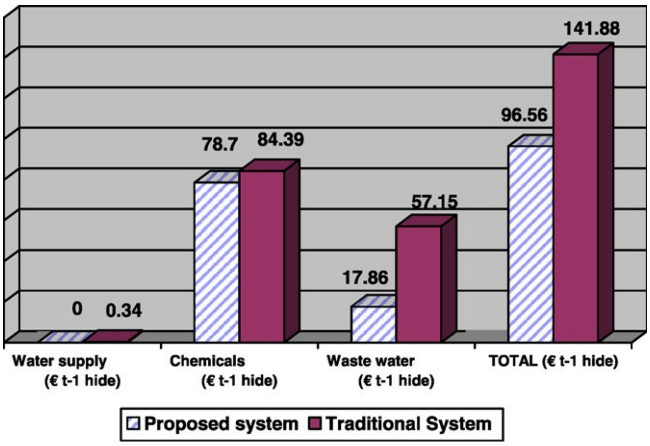

Fig. 4. Economical

Table 1
Low-salt content tanning formulation

(On split weight)			
Tanning	1.5% NaCl	Rotate – 15′	
	0.5% HCOOH (1:10)	Rotate – 30′	
	0.5% H_2SO_4 (1:10)	Rotate – 90′	
	2% chrome salt 33°Sch.		
	5.5% chrome salt 66°Sch.	Rotate – 2 h	
	0.15% MgO	Rotate – 4 h	
			T = 55 °C
			pH 3.8

Rest (24 h), drain, shave and weigh, neutralize (pH 5) and fatliquor.

Table 2
Traditional formulation

(On split weight)		
Tanning	70% H_2O	
	7% NaCl	Rotate – 15^{0}
	0.5% HCOOH (1:10)	Rotate – 30^{0}
	0.7% H_2SO_4 (1:10)	Rotate – 90^{0}
	2% chrome salt 33°Sch.	
	5.5% chrome salt 66°Sch.	Rotate – 2 h
	0.15% MgO	Rotate – 4 h
		T = 30 °C
		pH 3.8

Rest (24 h), drain, shave and weigh, neutralize (pH = 5) and fatliquor.